Electrochemical fabrication of ultra-low noise metallic nanowires with hcp crystalline lattice

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We experimentally demonstrate that low-frequency electrical noise in silver nanowires is heavily suppressed when the crystal structure of the nanowires is hexagonal closed pack (hcp) rather than face centered cubic (fcc). Using a low-potential electrochemical method we have grown single crystalline silver nanowires with hcp crystal structure, in which the noise at room temperature is two to six orders of magnitude lower than that in the conventional fcc nanowires of the same diameter. We suggest that motion of dislocations is probably the primary source of electrical noise in metallic nanowires which is strongly diminished in hcp crystals.

Metallic nanowires are integral components of several nanoscale electronic circuits, particularly in crossbar interconnect architectures.[1] Both experiments[2,3] and electrical modelling[4] have often addressed the effects of size on average electrical resistivity (ρ) of the nanowires, but very little is known about the low-frequency $1/f$-type electrical noise in these systems which can seriously impede their application in nanoelectronics.[5,6] Moreover, recent experiments suggest that the magnitude of noise in nanowires can indeed be much larger than that generally observed in thin polycrystalline metal films.[7] Hence our objective here is to address two issues: (1) what is the microscopic origin of low-frequency electrical noise in nanowires, and (2) can the noise in nanowires be suppressed or reduced by appropriate engineering of growth and structural parameters.

The power spectral density S_R of low-frequency $1/f$ noise in resistance R is normalized as,

$$S_R(f) = \frac{\gamma_H R^2}{N_e (f/Hz)^\alpha}$$

where N_e is the total number of electrons, and γ_H is the phenomenological Hooge parameter that depends on the material properties, such as nature and kinetics of disorder, scattering cross-section of electrons, crystallinity, and so on.[8,9] In thin polycrystalline metallic films, γ_H generally lies in the range $\sim 10^{-3} - 10^{-5}$, which is predominantly due to the migration of point defects along the grain boundaries.[10,11,12] Surprisingly though, the value of γ_H, in electrochemically grown single crystalline fcc silver nanowires (AgNWs) (≈ 15 nm diameter) was found to be very large ($\gamma_H \sim 10^{-1} - 10^{-2}$), even when the grain boundaries are expected to be absent. Although an explanation based on Rayleigh-Plateau instability has been proposed for narrow nanowires[7], the source of noise in wires of larger diameter (~ 100 nm) is not clearly understood. Moreover, whether other defect kinetics, such as thermally activated movement of dislocations,[13] contribute to the observed noise still remains uncertain.

The nature of crystallinity is known to have a profound influence on the kinetics of dislocations.[14] Since it is intimately connected to plasticity, a study of noise can also be relevant to understand the intrinsic structural aspects of the nanowires. Hence, to evaluate the role of defect kinetics on noise in nanowires, we have carried out detailed electrical characterization of single crystalline AgNWs in both fcc and hcp forms. We find that the value of γ_H, at room temperature ($T \approx 300$ K) in hcp AgNWs, is several orders of magnitude lower than that in fcc AgNWs, which indicates that dislocation motion may be the dominant source of electrical noise in metallic nanowires.

Although silver is fcc in bulk crystalline form, a competition between the surface and internal packing energies has been shown to stabilize the hcp structure in both nanoparticles[15] and nanowires[16] below certain critical dimensions. Conventional over-potential electrodeposition (OPD) technique, which employs inter-electrode potential (V_d) larger than the equilibrium Nernst potential (E_0) yields mainly fcc AgNWs, when the template pore size is more than 50 nm. Recently, a modified electrochemical route was suggested, where the growth takes place at $|V_d| \ll |E_0|$, with the resulting AgNWs stabilized entirely in the single crystalline hcp phase even for nanowire diameters as large as 100 nm.[17] Even though the precise growth mechanism for the latter, called the low-potential electrodeposition (LPED), is not well understood, the control on the crystal structure of the nanowires allows us to investigate electrical noise in nanowires of the same diameter and material, but different dislocation kinetics.

We have used polycarbonate templates (Whatman International Ltd.) with average pore size ≈ 60 nm and pore length 6 μm, which were coated with thin gold film on one side to serve as anode. By injecting electrolyte through a metallic micro-capillary (cathode) mounted on a vertical micropositioning stage, the AgNWs were locally electrodeposited over an area of about 1 mm^2 of the template under both LPED and OPD conditions. The selected area electron diffraction (SAED) patterns from similarly prepared nanowires, as shown in Fig. 1a and 1b, show the OPD AgNWs in expected fcc structure, while the LPED AgNWS in hcp phase (without any trace of fcc component, as confirmed by the X-ray

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diffraction (XRD) studies[17]). The time of local electrodeposition was optimized (20 mins) to allow a small overgrowth of mushroom heads, so that the contact resistance was extremely low ($\lesssim 0.2$ Ohms), when connected with conducting silver epoxy. The local electrodeposition was used to restrict the number of nanowires, and to ensure that the net resistance and noise are not too small to measure. Fig. 1c displays Scanning Electron Microscope image of a typical device without electrical contacts. The schematic of the electrical characterization set-up, which was used for both resistivity and noise measurements, is sketched in Fig. 1d. For the noise measurements, the device was included as one of the arms of a Wheatstone bridge, followed by amplification of the error signal, digitization and digital signal processing, which allows simultaneous measurement of background as well as bias dependent sample noise.[18] The apparatus can measure voltage power spectral densities as small as $10^{-21} \mathrm{V}^2/\mathrm{Hz}$. The details of data acquisition and digital signal processing are described elsewhere.[19]

In Fig. 2a we have summarized the result of conductance measurements on more than 100 devices, grown at V_d ranging over nearly five decades. In the LPED regime, the devices were generally stable for $|V_d| \gtrsim 10$ mV (yield $\sim 40 - 50\%$), but become progressively unstable as V_d was reduced, with the life time being as small as few hours. We did not find any specific trend in conductance as a function of V_d, probably due to the fluctuations in the number of nanowires from one device to the other, or any marked difference in the value of conductance for the nanowires grown in OPD and LPED conditions. To study the behavior of noise in the LPED regime, we have focused on AgNW device grown at $V_d = 100$ mV, although most of the other stable devices also showed qualitatively similar behavior.

To evaluate γ_H quantitatively, the number of nanowires in the device under study was estimated using the method outlined in Ref.[3]. We first fitted the $R - T$ data with Bloch-Grüneisen formula, which is shown in Fig. 2b and 2c for two typical OPD and LPED devices, respectively. The Debye temperature (Θ_D) was extracted as a fit parameter, and found to be 240 K for OPD and 225 K for the LPED nanowires, which are about $10-20\%$ higher than that of the bulk value ($\Theta_{D0} = 204$ K). Following the method described in Ref.[3], the number of nanowires in LPED and OPD devices were estimated as 28 and 140, respectively.

Fig. 3 illustrates the power-spectral density (S_R) in the LPED (Fig. 3a) and OPD (Fig. 3b) devices over nearly three decades of frequency (f) at different values of T, stabilized at better than ± 10 ppm. The background potential fluctuations (Johnson noise, amplifier noise etc.) were below 10^{-19} V^2/Hz during all the measurements. The noise power drops rapidly with decreasing T for fcc AgNWs, while it is nearly independent of T for hcp AgNWs. γ_H can be weakly frequency dependent if S_R deviates from pure power law over the observed frequency range, and for comparison, γ_H measured at 1 Hz, was

used. The temperature dependence of γ_H in Fig. 4a shows that at the room temperature, the absolute value of γ_H in fcc AgNWs is three orders of magnitude higher than that of hcp AgNWs, but becomes roughly equal at ~ 100 K. Measurements on a large number of LPED AgNW devices show that the noise in these systems at $T \approx 300$ K may vary with growth parameters, intrinsic disorder and thermal cycles. Nevertheless, the value of γ_H was always found to be much lower than that of the OPD devices, and expressed as the bands corresponding to the growth potential V_d in Fig. 4d.

The contribution of Rayleigh instability to noise in our AgNWs of diameter ~ 60 nm is expected to be negligibly small. Noise from pipe diffusion of defects along a dislocation line has been considered in single crystalline Aluminium,[20] but in such a case the LPED and OPD devices would probably display similar noise magnitudes. However, if the noise arises from motion of dislocations themselves then its suppression in LPED AgNWs can be attributed to less number of slip systems (only basal plane) in hcp crystal than fcc OPD systems.[14] The strong T-dependence of noise in OPD AgNWs can be understood through a thermally activated kinetics of dislocations under the influence of internal stresses generated during growth[21]. However, the weak T-dependence of noise in hcp nanowires indicates that activated kinetics, similar to that discussed by Dutta, Dimon and Horn[22], are unlikely to be applicable in this case. An understanding of this may be linked to the high-energy crystal structure of LPED AgNWs which drives these systems away from the thermal equilibrium. The motion of dislocation would then correspond to transition between metastable states that are separated by strong potential barriers,[23] and would occur only under the influence of internal stresses, rather than temperature fluctuations.

The residual resistivity ratio ($R_{300\mathrm{K}}/R_{4.2\mathrm{K}}$) for LPED AgNWs was generally much smaller than OPD devices (Figs. 2c and 2d), which indicates the presence of additional disorders, such as vacancy clusters, that can lock the dislocation motion by forming Cottrell atmosphere around the dislocations. This may result in further lowering of noise level in hcp nanowire.[14] To substantiate this, we show the temperature dependence of frequency exponent α for both LPED and OPD systems in Figs. 4b and 4c respectively. The magnitude of α is consistently slightly larger in the OPD devices, and approaches $\sim 1.3 - 1.4$ for temperatures above 200 K. Note that for long-range diffusion of the scattering species, α is expected to be 1.5, which has been demonstrated for dislocation dynamics under the long-range stress field during plastic deformation.[24]

In summary, we have demonstrated that the $1/f$-noise in metallic nanowires is highly crystal structure dependent, and the noise magnitude in hcp AgNWs fabricated by low potential electrodeposition process is far less than that of conventional fcc AgNWs. The lower noise magnitude in hcp nanowires could be attributed to the dislocation dynamics restricted only in the basal plane, and

also the locking of dislocation motion by point defects and high energy barriers.

Acknowledgement

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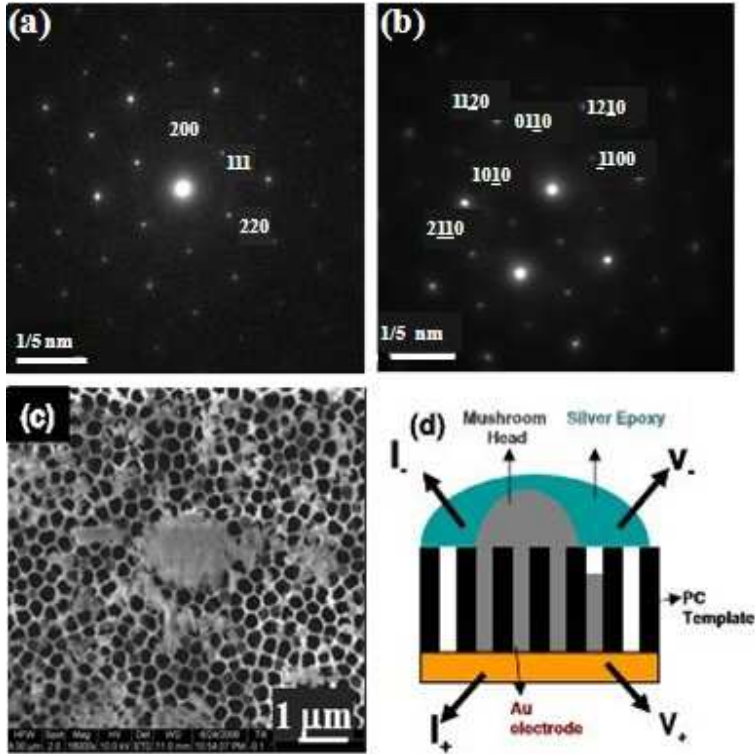[24] L.Laurson, and M. J. Alava, Phys. Rev. E **74**, 066106 (2006)

FIG. 1: Selective area electron diffraction (SAED) pattern of Silver nanowires (AgNWs) grown by (a) over potential electrodeposition (OPD) process, (b) low potential electrode-position (LPED) process, (c) Scanning Electron Microscope (SEM) image of AgNWs embedded in polycarbonate membrane showing mushroom heads, (d) schematic of contacted AgNWs for electrical characterization.
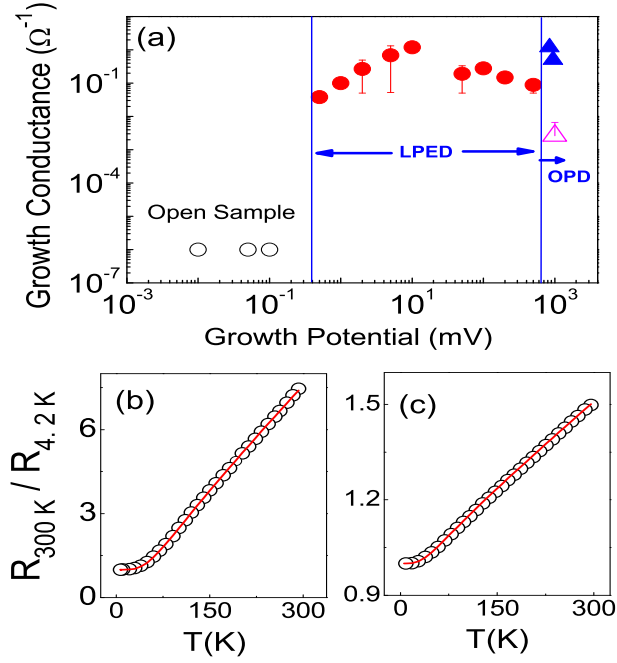
FIG. 2: (a) Growth-conductance vs growth-potential curve of as grown silver nanowires (AgNWs). Filled triangles correspond to the nanowires, grown by conventional OPD process and the open triangle corresponds to the AgNWs, grown at 1000 mV with the 2M electrolyte, (b) Resistance vs temperature $(R - T)$ curve of face centered cubic (fcc) AgNWs, (c) $R - T$ plot of Hexagonal closed packed (hcp) AgNWs. The open circles represent the experimental data while the solid line (red) shows the Bloch-Grüneisen fit to the experimental $R - T$ data.
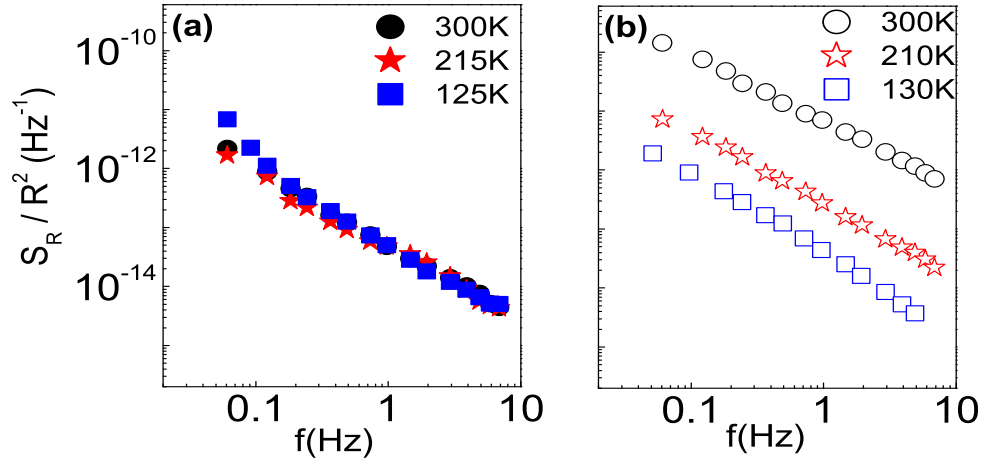
FIG. 3: Normalized power spectra vs frequency plot of (a) hcp silver nanowires (AgNWs) at temperatures 300 K, 215 K and 125 K, (b) fcc AgNWs at temperatures 300 K, 210 K and 130 K.
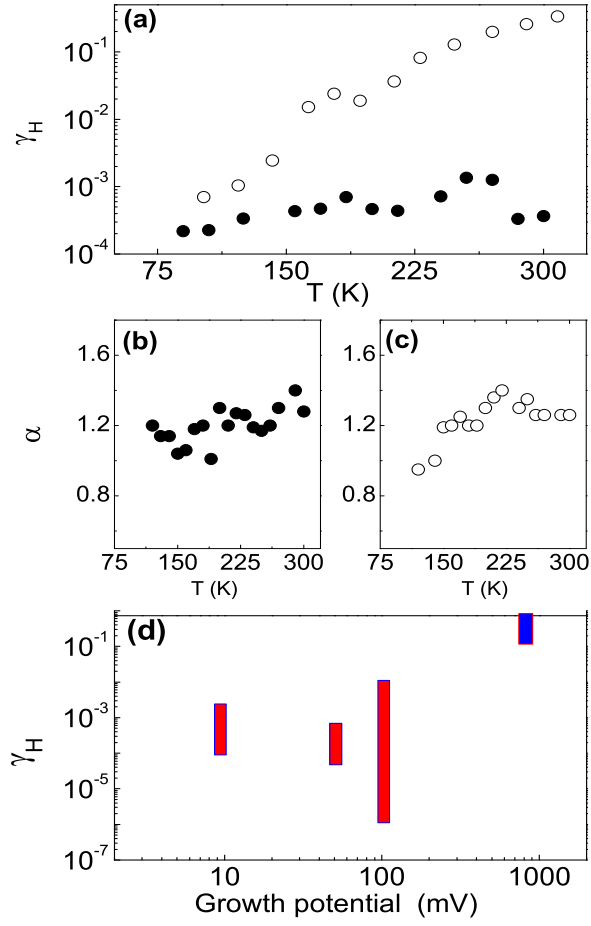
FIG. 4: Variation of (a) Hooge parameter γ_H ($f = 1$ Hz) with temperature for hcp nanowires (filled circle) and fcc nanowires (open circle), (b) frequency exponent α with temperature for hcp nanowires (filled circle) and fcc nanowires (open circle), (c) Hooge parameter γ_H, in the form of bands, with growth potential of as grown silver nanowires at room temperature.